PATENT APPLICATION

POLYMER-MODIFIED ASPHALT EMULSION

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of the filing of U.S. Provisional Patent Application Serial No. 60/152,399, entitled *Polymer-Modified Asphalt Emulsion*, filed on September 3, 1999, and the specification thereof is incorporated herein by reference.

BACKGROUND OF THE INVENTION

Field of the Invention (Technical Field):

The present invention relates to polymer-modified asphalt emulsions, and a method and apparatus to make and use the asphalt emulsions for repairing roads and pavement. More particularly, the invention relates to stable, asphalt polymer compositions that can be applied at ambient temperatures.

Background Art:

Often conventional asphalt does not retain sufficient elasticity during use, and, also, exhibits a plasticity range which is too narrow for use in many modern applications such as road construction. To overcome this problem, various polymers have been added to asphalt to improve physical and mechanical performance. The characteristics of road asphalt and the like can be greatly improved by incorporating an elastomeric type polymer, or a random or block copolymer of styrene and a conjugated diene. Consequently, polymer-modified asphalt is routinely used in the road construction/maintenance and roofing industries. Polymer-modified asphalt generally comprises styrene butadiene-based polymers, which have raised softening point, increased viscoelasticity, enhanced strain recovery, and improved low temperature strain characteristics. However, the technical challenge remains in producing a polymer modified asphalt or polymer asphalt emulsion that is stable for long periods of time, that will strongly bind to aggregate, and in the case of the emulsions, that can be easily applied at ambient temperatures.

The durability of road pavement is greatly enhanced by the addition of a polymer. The polymer is added for the purpose of reducing the heat sensitivity of the asphalt by increasing or extending the plasticity range, and increasing the resistance to deformation and the breaking point. It has also been shown that the performance of a properly selected asphalt polymer composition is superior to that of an asphalt not containing an added polymer. However, the problems of constituent compatibility encountered in attempts to obtain the best compromise between the performance and storage stability are difficult to overcome. European Patent EP458386 relates to a process for obtaining an asphalt polymer composition that is stable under conditions of fluidity prevailing during hot storage. The process consists of mixing at a temperature of 200 to 250°C, 85 to 98 weight percent of a selected asphalt, and 15 to 2 weight percent of a sequenced styrene/butadiene/styrene copolymer (SBS).

Polymer asphalt mixtures that are employed at the present time in heavy load applications, such as road construction and repair, often do not have the optimum characteristics at low enough polymer concentrations to consistently meet the increasing structural and workability requirements imposed on roadway structures in their construction. Common practice is to add the desired level of a single polymer, and a cross-linking agent, such as sulfur, until the desired asphalt properties are met. However, the relatively high cost of the polymer adds significantly to the overall cost of the resulting asphalt/polymer mix. Thus, it is highly advantageous to develop a polymer asphalt mix that is low in polymer concentration but still has the requisite properties. Due to the large quantities involved, cost factors weigh heavily in the practical application of any polymer asphalt mixture.

Grubba, U.S. Patent No. 5,795,929 appears to have overcome the high polymer/asphalt ratio and the incompatibility problems associated with prior polymer-modified asphalt emulsions. Grubba found that when sulfur is added as a cross-linking agent to an asphalt mixture containing both radial and linear styrene-diene copolymers (total 0.5-20 wt.%) significant property enhancements occur. Interestingly, no property enhancements were found in the absence of added sulfur. Asphalt emulsions can also be prepared utilizing Grubba's polymer modified mixture. In this case polymer-modified asphalt emulsions were prepared consisting of 60 to 80% asphalt polymer to 40 to 20% water, respectively, and an emulsifying agent. One disadvantage of the Grubba process is the need for an emulsification mill.

The emulsification mill operates at temperatures between 190° F to about 210°F, and slices the asphalt-polymer mix finely to mix it with the water to form the emulsion. The present invention does not require an emulsification mill, and the polymer modified asphalt emulsion can be prepared at ambient temperatures.

Asphalt emulsions are desirable in many applications because of improved handling and application at temperatures lower than hot/mix asphalt resulting from the presence of an asphalt solvent or carrier phase, for example, water. For example, hot/mix asphalt, and combinations of asphalt, aggregate and a single polymer, are commonly heated to, and applied at, a temperature of 350-450°F to achieve the requisite plasticity. In comparison, an asphalt emulsion is typically heated to, and applied at, temperatures between 130-170°F to achieve the same working characteristics.

A basic emulsification requires three components: asphalt, a carrier phase (e.g., water) and an emulsifying agent. A typical emulsion is formed through addition of asphalt, any desired performance-enhancing additives, an emulsifying agent and about 20-40 weight percent of water. Once the emulsion is applied, the water evaporates, leaving the asphalt structurally bound to the aggregate or other paving material. One advantage of water-based emulsified asphalt products is that they do not use or release volatile organic compounds in quantities associated with hot-mix asphalt. Hot-mix asphalt is generally diluted with hydrocarbon solvents such as diesel fuel or naphtha to improve the workability of the product during application.

Heightened environmental awareness has stimulated increased usage of emulsified asphalt in the road-paving industry. The type of emulsifier employed is determined by the desired application of the asphalt emulsion. In the case of rapid-set emulsions (mainly used for repair work of old pavement), the emulsion is applied on the existing surface and aggregate is spread on top. After the water from the emulsion has evaporated, an intimate mixture of asphalt and stone with good load-bearing capacity is formed. There are two basic types of emulsions: anionic emulsions and cationic emulsions. While nonionic emulsions also exist, they are used less frequently than anionic and cationic emulsions. The advantage of anionic emulsion lies in the relatively low cost of the emulsifying agents. However, as most

of the aggregates used are negatively charged, for example, quartz and granite, the electrostatic repulsion between the negatively charged asphalt emulsion and the negatively charged stones causes inferior adhesion. This results in the asphalt separating from the stones, or what is generally known as the asphalt/stripping problem. This problem is also encountered in hot/mix applications and when cutback asphalt is used.

The quality of the road surface is generally dependent upon the strength of the bonds between the asphalt and the aggregate after curing of the composition. Poor surface performance is due to poor adhesion, which results in asphalt stripping off the aggregate surface. Asphalt compositions also have relatively poor adhesion to aggregate in the presence of water, because the aggregate prefers to be wetted by the water rather than the asphalt. As a result, the water in the emulsion interferes with the bond between the aggregate and the asphalt. The result is the formation of potholes. To reduce water-induced debonding of asphalt from the stone surface, it is common to add surface-active amines or diamines to the asphalt. The patent literature sets forth a large number of compounds that can be used to improve adhesion of asphalt to aggregate. See, e.g., Schilling, U.S. Patent No. 5,667,578.

The present invention provides a polymer-enhanced asphalt that can be applied at ambient temperature. The present invention also provides an improved mechanical stirring apparatus.

SUMMARY OF THE INVENTION (DISCLOSURE OF THE INVENTION

The present invention is directed to a polymer-modified asphalt emulsion and a mixing/stirring/blending apparatus particularly useful for road and pavement repairs and potholes. The polymer-modified asphalt emulsion comprises bitumen, a block copolymer comprising styrene, a rosin ester and a cationic asphalt emulsion. The mixture can be applied at ambient temperature.

The preferred block copolymer comprising styrene is styrene-butadiene-styrene (SBS), although other block copolymers may be utilized in accordance with the invention. The block copolymer may be present in powdered form. The emulsion preferably comprises between approximately 0.5 and 20

percent by weight of SBS and most preferably between approximately 2 and 15 percent by weight of SBS.

The bitumen preferably has a petroleum asphalt pen number of 10mm penetration. The emulsion preferably comprises between approximately 2 and 6 percent by weight bitumen and most preferably between approximately 4 and 5 percent by weight bitumen.

The rosin preferably comprises a high acid number and is preferably dimerized. The emulsion preferably comprises between approximately 0.02 and 2 percent by weight rosin and most preferably between approximately 1 and 2 percent by weight rosin.

The emulsion preferably comprises between approximately 20 and 40 percent by weight of water and most preferably between approximately 30 and 35 percent by weight of water.

The cationic asphalt emulsion preferably comprises an amine, such as a quatenary amine and an emulsifying agent, such as amines, primary amines, diamines, quatenary amines, imidazolene amines and combinations thereof. Preferred emulsifying agents include, but are not limited to, imidazoline dodecyl phenol, quatenary diamine phenol and combinations thereof. The emulsion preferably comprises between approximately 50 and 80 percent by weight of cationic emulsion and most preferably between approximately 60 and 70 percent by weight of cationic emulsion.

In an alternative embodiment, the emulsion further comprises an additional amine which is added to the bitumen/rosin reaction. The emulsion preferably comprises between approximately 0.2 and 0.3 percent by weight. The preferred additional amine is ditaloamine.

The invention further comprises a method of making a polymer-enhanced asphalt emulsion, comprising: a) mixing a block copolymer comprising styrene, rosin, and bitumen; b) heating the block copolymer/rosin/bitumen mixture; and c) mixing the block copolymer/rosin/bitumen mixture with cationic asphalt emulsion.

In the preferred embodiment, the block copolymer and rosin are mixed to form a dry mixture and then this dry mixture is added to the bitumen. The block copolymer may be powdered.

The preferred compositions and reactants are discussed above. The mixture may be applied at ambient temperature to the surface being repaired.

The present invention also is directed to a mixer/stirrer/blender apparatus comprising a shaft, a plate or blade with at least one opening in the blade. Preferably, there are a plurality of plates (most preferably three plates), and a plurality of openings in at least two of the plates. Preferably there are no openings in the central plate. The plates are preferably circular. For certain applications (e.g. use in a 55-gallon drum), the plates preferably comprise an approximately five-inch radius.

The openings in the plates are preferably circular. Preferably, there are four openings in each plate (that has openings). Preferably, each opening is spaced at a ninety-degree angle from its neighboring opening with respect to a center of the plate; centers of the four openings are located at a point approximately seventy percent of a distance from a center of the plate to an edge of the plate; and a radius of each of the four openings is approximately twenty percent of a distance from a center of the plate to an edge of the plate.

There are spacers on the shaft interposed between the plurality of plates. These spacers are preferably approximately 1/8 inch thick.

The apparatus prevents shear of the mixture being processed.

A primary object of the present invention is to provide a polymer-enhanced asphalt that can be applied at ambient temperature to selected aggregate to pave or repair roads, pavement or other surfaces.

A further object of the invention is to provide an asphalt emulsion with improved characteristics for handling, storage, and application.

A further object of the invention is to provide an asphalt emulsion that is applied at ambient temperatures with minimal release of volatile organic compounds (VOC) into the environment.

Another object of the invention is to provide an improved stirring/mixing/blending apparatus.

A primary advantage of the present invention is the storability of the polymer-enhanced asphalt emulsion.

Another advantage of the present advantage is the high degree of bonding between the asphalt emulsion and the aggregate.

Another advantage of the present advantage is that the mixture can be varied over a wide compositional range depending on the application.

Another advantage of the present invention is the uniform appearance of the asphalt-aggregate patch to the unrepaired portion of the road or pavement.

Other objects, advantages and novel features, and further scope of applicability of the present invention will be set forth in part in the detailed description to follow, taken in conjunction with the accompanying drawings, and in part will become apparent to those skilled in the art upon examination of the following, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the specification below.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated into and form a part of the specification, illustrate several embodiments of the present invention and, together with the description, serve to explain the principles of the invention. The drawings are only for the purpose of illustrating a preferred embodiment of the invention and are not to be construed as limiting the invention. In the drawings:

Fig. 1 is a diagram of one of the outer stirrer blades of the mechanical stirring apparatus of the invention;

Fig. 2 is a component diagram of the mechanical stirring apparatus; and

Fig. 3 is a chemical structural representation of the rosin (Sylvaros PR 295) preferably used in the emulsification process of the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS (BEST MODES FOR CARRYING OUT THE INVENTION)

The present invention is of a polymer-enhanced asphalt emulsion comprising bitumen (e.g., bitumen (AC-10) from Frontier, Cheyenne, Wyoming wherein the 10 stands for a petroleum asphalt pen number of 10 for a 10mm penetration, standard test), a block polymer comprising styrene (e.g. styrene-butadiene-styrene (SBS)), a rosin ester with high acid number (e.g. Sylvaros PR-295 (chemical structure illustrated in Fig. 3) from Arizona Chemical Company, Panama City, Florida), and a cationic asphalt emulsion. Of course, other types of styrene containing block polymers known in the art may be suitable in lieu of or in addition to SBS block copolymers, for example, but not limited to styrene-ethylene-butylene-styrene (SBES) block copolymer. The term "SBS block polymer", as used throughout the specification and claims, is intended to include all styrene containing block polymers or copolymers.

As used throughout the specification and claims, the terms "bitumen" and "asphalt" are used interchangeably. The SBS block polymer is preferably mixed with the rosin to form a dry mixture.

The rosin is preferably a high acid number rosin ester and preferably dimerized. The rosin preferably ranges between approximately 0.02 percent by weight and 2 percent by weight, and most preferably between approximately 1 percent by weight and 2 percent by weight.

The dry mixture is slowly added to the heated asphalt, and heated for preferably one to two hours at 300° F - 500° F. The heated asphalt-polymer is then added to an already prepared cationic asphalt emulsion at ambient temperature. With the specialized mixer blade of the invention, the asphalt-polymer mixes almost immediately with the asphalt emulsion with no separation or incompatibility problems observed.

The emulsion comprises some water, dependent upon the desired flow and cure characteristics of the final mixture. The quantity and type of emulsifying agent used are dictated by the desired use of the emulsion. Other molecules comprising hydroxyl groups may also be added to adjust characteristics of the emulsion. The quantity and type of emulsifying agent used in the present invention are consistent with existing asphalt and polymer-modified emulsions known in the art. Known cationic emulsifying agents that can be used in the present invention include chemical agents and clay agents. Chemical agents include, but are not limited to, nitrogen containing molecules, such as, but not limited to, amines, for example, but not limited to, primary amines, secondary amines, quaternary amines, monoamines, diamines and other polyamines. Clay agents comprise clays, such as, but not limited to, bentonite clays and the like. In particular, imidazoline dodecyl phenol and quatenary diamine phenol are used separately or in combination. The cationic emulsion preferably ranges between 50-80 percent by weight, and most preferably between approximately 60-70 percent by weight.

For the present invention, the amount of water in the final polymer-modified asphalt emulsion preferably ranges between approximately 20 and 40 percent by weight and most preferably approximately 32 percent by weight. The preferred weight percent of SBS in the final asphalt polymer emulsion preferably ranges between approximately 2 percent by weight and 20 percent by weight, and most preferably approximately between approximately 2 percent by weight and 15 percent by weight.

The final asphalt mixture can be stored in a sealed container for at least six (6) months, perhaps longer, and used as needed.

In an alternative embodiment, the asphalt emulsion further comprises an additional amine, preferably a di-tallow quaternary amine, for example, but not limited to, DTDMAC (di-tallow, di-methyl ammonium chloride) or di-tallow amine. This amine is in addition to the amine in the cationic emulsion. This amine is added, in a small amount, to the rosin/bitumen/SBS reaction to allow particles to better or completely disperse when in the mixer apparatus of the present invention. The additional amine is present in an amount of preferably between approximately 0.2 percent by weight and 0.3 percent by weight.

The invention additionally comprises methods to repair potholes and cracked pavement, especially employing the composition of the invention described above. An example of the method when used to repair a pot hole approximately three to four inches in depth follows: The pothole is filled with approximately 3/8 inch washed silicious aggregate or other paving or surfacing material. Deeper pot holes are filled with larger, washed aggregate provided that approximately 3/8 inch aggregate is layered atop the larger aggregate. The prepared asphalt polymer emulsion, the composition of the present invention, is poured into the aggregate filled hole to a level approximately equal to that of the pavement. A small amount of additional 3/8 inch aggregate may be added to the hole. After approximately twenty to thirty minutes the asphalt/aggregate mixture is cured to the point such that the mixture can be compressed and leveled with the pavement, resulting in a patch that is uniform in appearance to the unrepaired portion of the roadway pavement.

As to cracked pavement, for pavement cracks less than approximately one (1) inch in width, the crack is preferably routed with a commercial pavement router to at least one (1) inch in width, cleared of loose sand or gravel, and filled with approximately 1/8 to 1/4 inch washed silicious aggregate. The fill step is repeated as in the case of repairing the pothole, above.

Referring to Figs. 1 and 2, the invention additionally comprises a mechanical stirrer/mixer/blender that is used to mix the polymer/rosin mix with the asphalt and later used to mix the asphalt polymer mixture with the cationic asphalt emulsion. This facilitates the mixing of these respective components to a point achieving approximate homogeneity. The stirrer preferably comprises a shaft **10**, a plurality of stirrer blades **14**, and a plurality of spacers **12**. The shaft **10** may be disposed in any container (e.g. a 55-gallon drum) for conducting the mixing on site. An electric drill can be used to drive the shaft **10**.

The stirrer preferably has three stirrer blades. The blades are preferably approximately 1/4 inch thick and preferably disposed on top of each other with 1/8 inch washers or spacers. A useful material for the blade is aluminum, but other materials may be utilized. The blades are preferably circular with a radius of approximately five (5) inches. The stirrer blades are attached to one end of the shaft **10**. Each outer blade **14** preferably has circular openings **16** (e.g. four openings), ninety degrees from one another, that are preferably centered 3 1/2 inches from the center of the blade **18**. Preferably, the diameter of the openings is approximately 2 inches.

Although circular openings are shown in the drawings, oval openings could be utilized. The purpose of circular or oval openings is to avoid shear. When the liquid enters the hole, it acts as a pump and pumps the liquid over the surface of the blade. An opening of sharp edges (e.g. square openings) may cause shear. Radial velocity is used to achieve the pumping and stirring of the mixture. Likewise the blades may have more or less than four openings.

<u>Industrial Applicability</u>:

The invention is further illustrated by the following non-limiting examples.

<u>Example 1 (3.0% SBS)</u>

Bitumen (43 lbs., AC-10, Frontier, Cheyenne, Wyoming) was heated to a temperature of between approximately 300° F and 500° F. Powdered SBS with a typical molecular weight (M_w) of 1 to 1.5 million (8.6 lbs., 31/69 S/B ratio, Dexco Polymers, Houston Texas) was mixed with a rosin-ester with high acid number (0.45 lbs., Sylvaros PR 295, Arizona Chemical Co.). The polymer/rosin mixture was slowly

added with gentle stirring using the mixing/stirring apparatus of the present invention to the bitumen at approximately 300° F to 500° F. until all the polymer/rosin mixture was added. The polymer asphalt mixture was maintained at approximately 300° F to 500° F for one to two hours and then mixed with the mixer/stirrer of the invention. The heated polymer asphalt mixture was then added to approximately thirty (30) gallons of already prepared cationic asphalt emulsion at ambient temperature. The polymer-asphalt emulsion was rapidly mixed (approximately 300 to 600 rpm) with the mixer/stirrer for ten minutes.

<u>Example 2 (4.0% SBS)</u>

The same preparation method was used as described for Example 1 for the corresponding amounts of materials:

Bitumen:	43 lbs
SBS:	12.5 lbs.
Rosin:	0.625 lbs.
Asphalt Emulsion:	30 gallons

<u>Example 3 (5.0% SBS)</u>

The same preparation method was used as described for Example 1 for the corresponding amounts of materials:

Bitumen:	43 lbs.
SBS:	17.2 lbs.
Rosin:	0.96 lbs.
Asphalt Emulsion:	30 gallons

<u>Example 4 (6.0% SBS)</u>

The same preparation method was used as described for Example 1 for the corresponding amounts of materials:

Bitumen:	50 lbs
SBS:	19.0 lbs.
Rosin:	1.0 lbs.
Asphalt Emulsion:	30 gallons

<u>Example 5</u>

The mixture of Example 1 was tested to repair a pothole. After 11 months to-date, the asphalt mixture of the present invention remains in good condition, with no evidence of shrinkage, cracking, sinking or other wear.

<u>Example 6</u>

The mixture of Example 4 was tested to repair a pothole. After 8 months, to-date, the asphalt mixture of the present invention remains in good condition, with no evidence of shrinkage, cracking, sinking or other wear.

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples. In particular, the weight percent of SBS in the final asphalt polymer emulsion can vary from approximately 2% to approximately 20%, and the corresponding weights and volume of the other constituents adjusted accordingly.

Although the invention has been described in detail with particular reference to these preferred embodiments, other embodiments can achieve the same results. Variations and modifications of the present invention will be obvious to those skilled in the art and it is intended to cover in the appended

claims all such modifications and equivalents. The entire disclosures of all references, applications, patents, and publications cited above are hereby incorporated by reference.